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(54) Title: WATER EXTRACTION OF HYDROGEN FLUORIDE FROM A HALOCARBON/HYDROGEN FLUORIDE AZEOTROPIC MIXTURE

(57) Abstract

A process for the separation of mixtures containing halocarbons and hydrogen fluoride. Either water alone or a blend comprising water and hydrogen fluoride is added to a mixture comprising a halocarbon and hydrogen fluoride to thereby form a first phase rich in the halocarbon and a second phase rich in hydrogen fluoride and water. The most preferred halocarbon is 1,1,1,3,3-pentafluoropropane. Preferably the first and second phases are then separated. Optionally the second phase rich in hydrogen fluoride and water is also separated.

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WATER EXTRACTION OF HYDROGEN FLUORIDE FROM A HALOCARBON/HYDROGEN FLUORIDE AZEOTROPIC MIXTURE

BACKGROUND OF THE INVENTION

FIELD OF THE INVENTION

The present invention pertains to a process for the separation of a halocarbon and hydrogen fluoride from a mixture of the halocarbon and hydrogen fluoride. More particularly, the invention relates to the separation of azeotropic mixtures of halocarbons and hydrogen fluoride. Preferably the halocarbon contains three or more carbon atoms and most preferably is a hydrofluorocarbon.

DESCRIPTION OF THE PRIOR ART

It is well known in the art to react hydrogen fluoride with various compounds in order to produce fluorinated halocarbons or fluorocarbons (HFCs). Such halocarbons are useful as solvents, refrigerants, blowing agents and aerosol propellants, among other uses. Hydrofluorocarbons (HFC's) are a preferred class of halocarbons since they are considered to be much more environmentally advantageous than halocarbons such as

hydrochlorofluorocarbons (HCFC's) or chlorofluorocarbons (CFC's) since they are essentially non-ozone depleting, non-flammable and non-toxic as compared to chlorine containing chlorocarbons. In the production of fluorocarbons, a typical product stream contains unreacted hydrogen fluoride, other starting reagents and by-products as well as the desired HFC. Various conventional separation techniques, for example distillation and scrubbing may separate certain by-products and starting materials from a product stream, however, particular difficulty can be experienced in removing halocarbons, including hydrofluorocarbons from hydrogen fluoride. This is especially true for those hydrofluorocarbons having boiling points close to that of HF. In a typical method of preparing hydrofluorocarbons, precursor reagents are fluorinated with hydrogen fluoride. It would be desirable to produce substantially pure hydrofluorocarbons, however, this has proved to be difficult since many hydrofluorocarbons, especially hydrofluorocarbons having three or more carbon atoms, and hydrogen fluoride form azeotropic mixtures which are substantially inseparable by distillation.

The prior art has suggested various methods of separating azeotropic mixtures of hydrofluorocarbons. In this regard European patent application EP 0 472 391 suggests separating HFC-134a from a mixture with chlorine containing hydrochlorofluorocarbons using an extraction agent such as trichloroethylene or perchloroethylene. European patent application EP 0 467 531 teaches a method of separating HFC-134a from a mixture of HFC-134a with HF by passing the mixture through a distillation column to separate the

mixture form a residue of pure HFC-134a and then collecting the residue. European patent publication EP 0 583 551.A1 uses HF to extract HF from a HFC-134a/HF azeotrope. HFC-134a is a two carbon fluorocarbon. U.S. patent 5,211,817 attempts a separation of fluorocarbons from azeotropic mixtures with HF by column distillation and withdrawing a vapor sidestream followed by introducing the sidestream into a rectifying column equipped with a condenser and operated at a high reflux ratio. Sulfuric acid has been used heretofore to separate a gaseous mixture of HF from a chlorine containing chlorofluorocarbon, namely FC-22 as described in U.S. patent 3,873,629. U.S. 3,947,558 recovers HF from C_1 - C_3 halocarbons using a monoglycol. These provide less than satisfactory solutions to the problem.

According to the preferred form of the present invention there is provided a method for separating a hydrofluorocarbon and hydrogen fluoride from a mixture of the hydrofluorocarbon and hydrogen fluoride by using either water alone or a water/HF mixture as an extracting agent. Although water/HF azeotropic compositions are well known, their use as an extracting agent for the separation of HF from halocarbons such as those which contain three or more carbon atoms is not known. In addition, the use of water as an HF extracting agent for halocarbon is not known.

SUMMARY OF THE INVENTION

The invention provides a process for separating a halocarbon and hydrogen fluoride from a mixture containing a halocarbon and hydrogen fluoride which comprises adding a blend comprising water and hydrogen fluoride to a mixture comprising a halocarbon and hydrogen fluoride to thereby form a first phase rich in the halocarbon and a second phase rich in hydrogen fluoride and water; wherein the weight ratio of water to hydrogen fluoride in the added blend ranges from about 2:3 to about 4:1 and wherein the weight ratio of water to hydrogen fluoride in the formed second phase ranges from about 1:3 to about 1:1.

The invention also provides a process for separating a halocarbon and hydrogen fluoride from a mixture containing a halocarbon and hydrogen fluoride which comprises adding water alone to a mixture comprising a halocarbon and hydrogen fluoride to thereby form a first phase rich in the halocarbon and a second phase rich in hydrogen fluoride and water; wherein the weight ratio of added water to hydrogen fluoride ranges from 3:2 to about 1:5 and wherein the weight ratio of water to hydrogen fluoride in the formed second phase ranges from about 3:2 to about 1:5.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

In the process of the instant invention, one commences with a mixture comprising a halocarbon and hydrogen fluoride. The mixture may be an azeotrope, but this condition is not necessary. In the preferred embodiment, the halocarbon is a fluorocarbon. More preferably, the halocarbon has three or more carbon atoms, and most preferably three or four carbon atoms. As used in this invention, the term fluorocarbon means compounds containing atoms only selected from carbon, hydrogen and fluorine. Such do not contain other halogen atoms. The fluorocarbon may be, for example pentafluoropropane, such as 1,1,1,3,3-pentafluoropropane which is also known as HFC-245fa or 1,1,2,3,3-pentafluoropropane which is also known as HFC-245ea. HFC-245fa is itself well known in the art as described in U.S. patent 2,942,036, Canadian 684,687, EP 381 986A, JP 02,272,086 and WO 95/04022. All of the foregoing patents are incorporated herein by reference. The process is also particularly useful for separating hydrogen fluoride from 1,1,1,2,2,5-hexafluorobutane, which is also known as HFC-356 mcfq.

In a first embodiment of the invention, one begins with a mixture of the halocarbon and hydrogen fluoride and then adds a blend of water and hydrogen fluoride to the mixture. In the first process for separating a halocarbon and hydrogen fluoride from a mixture containing a halocarbon and hydrogen fluoride, a blend comprising water and hydrogen fluoride is added to a mixture comprising a halocarbon and hydrogen fluoride to form a

first phase rich in the halocarbon and a second phase rich in hydrogen fluoride and water. The blend of water and hydrogen fluoride is preferably an azeotropic blend and more preferably a binary azeotrope. Upon the addition of the water/HF blend to the halocarbon/HF mixture, the hydrogen fluoride is concentrated in a second phase. That is, hydrogen fluoride from the halocarbon/hydrogen fluoride mixture leaves the mixture and becomes more concentrated in the HF/water. In effect the HF/water blend is a stronger azeotrope than the halocarbon/hydrogen fluoride mixture. The amount of HF/water blend needed for the separation depends on the amount of HF present in the system.

In the preferred embodiment, the weight ratio of water to hydrogen fluoride in the blend ranges from about 2:3 to about 4:1. More preferably the weight ratio ranges from about 2:3 to about 2:1 and most preferably from about 2:3 to about 1:1. The same ratios pertain in the invention embodiment wherein the halocarbon has at least three carbon atoms. Preferably the extraction is conducted at a temperature of from about 0 °C to about 100°C, more preferably from about 0 °C to about 40 °C, and most preferably from about 20 °C to about 40 °C. The extraction is usually conducted at normal atmospheric pressure, however, higher or lower pressure conditions may be used by those skilled in the art. Upon adding the HF/water blend to the mixture of fluorocarbon and HF, two phases rapidly form. A first phase is formed which is rich in the fluorocarbon and a second phase which is rich in HF/water. By the term "rich" is meant, the phase contains more than 50% of the indicated component in that phase, and preferably more than 80% of the indicated

component in that phase. In the preferred embodiment, the weight ratio of water to hydrogen fluoride in the resulting second phase ranges from about 1:3 to about 1:1, preferably from about 1:3 to about 2:3 and most preferably from about 1:3 to about 3:7.

After the separation of the phases, one removes the phase rich in the fluorocarbon from the phase rich in the hydrogen fluoride and water. This may be done by decanting, siphoning, distillation or other techniques well known in the art. One may optionally repeat the fluorocarbon extraction by adding more water/HF blend to the removed first phase. One may optionally thereafter separate the hydrogen fluoride and water by means well known in the art. For example, one can heat the concentrated HF/water phase at temperatures of up to 150°C to recover HF. The HF may then be recycled to a fluorocarbon formation step and preferably, the diluted water/HF blend is also recycled to extract more HF. In a preferred embodiment of the invention provides a process for separating a mixture of a halocarbon having at least three carbon atoms and hydrogen fluoride. This is done by adding a blend comprising water and hydrogen fluoride to the mixture. A first phase rich in the halocarbon and a second phase rich in hydrogen fluoride and water. The weight ratios of water to hydrogen fluoride and other conditions are given above for the blend and in the resulting second phase are given above.

In another embodiment of the invention, water alone is used as the extractant. When water alone is used as the extractant, the amount of water may be that amount effective to

remove HF from the mixture of halocarbon and hydrogen fluoride, and may be used in an excess amount. In the preferred form of this embodiment, the halocarbon has at least three carbon atoms and preferably three, four or five carbon atoms. The weight ratio of added water to hydrogen fluoride ranges from about 3:2 to about 1:5. More preferably the weight ratio ranges from about 3:2 to about 1:4 and most preferably from about 3:2 to about 1:3. In the preferred embodiment, the separating is conducted at the temperatures mentioned above. Also in the preferred embodiment, the mixture of halocarbon and hydrogen fluoride, the blend of water and hydrogen fluoride and the formed second phases are all azeotropic mixtures. In the preferred embodiment, the weight ratio of water to hydrogen fluoride in the resulting second phase also ranges from about 3:2 to about 1:5, more preferably the weight ratio ranges from about 3:2 to about 1:4 and most preferably from about 3:2 to about 1:3.

After the separation of the phases, one removes the phase rich in the fluorocarbon from the phase rich in the hydrogen fluoride and water. This may again be done by decanting, siphoning, distillation or other techniques well known in the art. One may optionally repeat the fluorocarbon extraction by adding more water or water/HF blend to the removed first phase. Optionally one may thereafter separate the hydrogen fluoride and water by means well known in the art. The HF may then be recycled to the fluorocarbon formation step and preferably, the diluted water/HF blend may also recycled to extract more HF.

The following non-limiting examples serve to illustrate the invention.

EXAMPLE 1

54 g of an azeotropic mixture containing about 71 wt. % HF and about 29 wt. % of HFC-356 mcfq were contacted with 55 g of an azeotropic blend containing about 42 wt. % HF and about 58 wt. % water and two phases formed immediately. An organic rich phase was formed which was composed of essentially all of the HFC-356 mcfq and only 0.67 wt. % HF and a moisture content of 466 ppm. A second phase contained approximately 67.7 wt.% HF, 0.33 wt.% organics and the balance water. From the material balance, the extraction efficiency is calculated, within experimental error, to be 102%. This experiment was done at room temperature (25 °C). The HF concentration was determined by ion chromatography.

EXAMPLE 2

78.7 g of an azeotropic mixture containing about 74 wt. % of HFC-245fa and about 26 wt. % of HF is contacted with 69.68 g of an azeotropic blend containing about 37.2 wt. % HF and the balance water and two phases form immediately. An organic rich phase was formed which was composed of essentially all of the HFC-245fa and only 0.1 wt. % HF. A second phase contained approximately 49.7 wt. % wt.% HF, and the balance

water. From the material balance, the extraction efficiency is calculated, within experimental error, to be 96%. This experiment was done at room temperature (25 °C). The HF concentration was determined by ion chromatography.

EXAMPLE 3

Binary compositions containing solely HFC-245fa and HF are blended to form a homogeneous azeotrope mixture. The vapor pressures of the mixtures as a function of compositions (wt.% HF) are measured at 20 °C and 75 °C and the following results are noticed.

TABLE 1

WEIGHT PERCENT HF	PRESSURE (PSIA)	
	T = 20 °C	T = 75 °C
0.0	17.6	100.3
8.3	25.3	138.9
19.9	26.2	141.8
23.1	26.3	141.6
32.7	26.1	138.9
39.5	26.1	136.6
47.9	25.8	133.3
100.0	14.9	81.4

The data show that the vapor pressure of mixtures of HFC-245fa and HF is higher, at all indicated blend proportions, than HFC-245fa and HF alone, i.e. as indicated in the first and last rows when HF is 0.0 wt.% and HFC-245fa is at 100.0 wt.% as well as when HFC-245fa is at 0.0 wt.% and HF is at 100.0 wt. %. The data also show that the azeotropic compositions (the composition at which the pressure is maximum) at 20 °C is about 23.1 wt.% HF (between 19.9 and 32.7 wt.% HF), and 75 °C is about 19.9 wt.% HF (between 8.3 and 23.1 wt.% HF). The vapor - liquid equilibrium of the mixtures are measured at temperatures of from about 20 °C and 75 °C and the following results are noticed.

TABLE 2

TEMPERATURE °C	PRESSURE (PSIA)	COMPOSITIONS (WEIGHT PERCENT HF, ± 3%)	
		LIQUID	VAPOR
19.8	25.8	48.3	27.8
74.6	132.8	53.0	24.5
19.8	26.1	32.7	27.5
19.8	26.2	20.2	23.9
74.6	141.8	15.9	16.2

A comparison of the data from Tables 1 and 2 indicates that the vapor - liquid equilibrium results from Table 2 are in agreement the vapor pressure measurements of Table 1.

EXAMPLE 4

Binary compositions containing solely HFC-356 mcfq and HF are blended to form a homogeneous azeotrope mixture. The vapor pressures of the mixtures as a function of compositions are measured at -0.4 °C, 19.8 and 60.1 °C and the following results are noticed.

TABLE 3

Vapor Pressure Measurement of HFC-356 mcfq/HF

WEIGHT PERCENT HFC-356 mcfq	PRESSURE (PSIA)	
	T = -0.4 °C	T = 19.8 °C
0.0	7.01	14.87
2.09	7.04	14.91
5.42	7.05	15.05
8.90	7.10	15.15
12.46	7.11	15.26
16.53	7.15	15.34
18.92	7.14	15.39
22.24	7.18	15.47
30.06	7.18	15.53
33.81	7.16	15.55
37.19	7.13	15.53

TABLE 4

Vapor Pressure Measurement of HFC-356 mcfq/HF

WEIGHT PERCENT HFC-356 mcfq	PRESSURE (PSIA)		
	T = -0.4 °C	T = 19.8 °C	T=60.1 °C
100.0	2.22	5.64	25.42
78.54	6.33	14.40	57.18
68.81	6.60	14.92	58.37
57.19	6.86	15.30	59.00
46.60	7.00	15.52	58.89
38.19	7.11	15.58	58.68

TABLE 5

Vapor- Liquid Equilibrium of HFC-356 mcfq /HF

TEMPERATURE (°C)	PRESSURE (PSIA)	WT.% HFC-356 mcfq (± 3%)		WT. % HFC-356 mcfq LOADED
		LIQUID	VAPOR	
-0.4	7.0	41.8	41.3	37.2
19.8	15.58	40.2	41.3	37.2
-0.4	7.0	35.2	30.6	32.6
19.8	15.45	33.3	35.7	32.6

The data show that the vapor pressure of mixtures of HFC-356 mcfq and HF is higher, at all indicated blend proportions, than HFC-356 mcfq and HF alone, i.e. as indicated in the when HF is 0.0 wt.% and HFC-356 mcfq is at 100.0 wt.% as well as when HFC-356 mcfq is at 0.0 wt.% and HF is at 100.0 wt.%. The data also show that the azeotropic composition (the composition at which the vapor pressure is maximum) is about 40± wt.% HF. The vapor-liquid equilibrium (VLE) of the HFC-356 mcfq/HF mixtures are measured at the temperature of about 0 °C and 20 °C, and the results are reported in Table 5. A comparison of the data from Tables 3, 4 and 5 indicates that the vapor - liquid equilibrium results are in agreement the vapor pressure measurements.

What is claimed is:

1. A process for separating a halocarbon and hydrogen fluoride from a mixture containing a halocarbon and hydrogen fluoride which comprises adding a blend comprising water and hydrogen fluoride to a mixture comprising a halocarbon and hydrogen fluoride to thereby form a first phase rich in the halocarbon and a second phase rich in hydrogen fluoride and water; wherein the weight ratio of water to hydrogen fluoride in the added blend ranges from about 2:3 to about 4:1 and wherein the weight ratio of water to hydrogen fluoride in the formed second phase ranges from about 1:3 to about 1:1.

2. The process of claim 1 wherein the halocarbon contains at least three carbon atoms.

3. The process of claim 2 wherein the halocarbon is a hydrofluorocarbon.

4. The process of claim 3 wherein the hydrofluorocarbon has three carbon atoms.

5. The process of claim 3 wherein the hydrofluorocarbon has four carbon atoms.

6. The process of claim 3 wherein the hydrofluorocarbon has five carbon atoms.

7. The process of claim 1 wherein the halocarbon comprises 1,1,1,3,3-pentafluoropropane.

8. The process of claim 1 wherein the halocarbon comprises 1,1,2,3,3-pentafluoropropane.

9. The process of claim 1 wherein the halocarbon comprises 1,1,1,2,2,5-hexafluorobutane.

10. The process of claim 1 wherein the blend of water and hydrogen fluoride is a binary azeotrope.

11. The process of claim 1 further comprising the subsequent step of removing the first phase rich in the halocarbon from the second phase rich in the hydrogen fluoride and water.

12. The process of claim 11 further comprising the subsequent step of separating the hydrogen fluoride and water in the second phase.

13. The process of claim 1 wherein the separating is conducted at a temperature of from about 0 °C to about 100 °C.

14. The process of claim 1 wherein the mixture of halocarbon and hydrogen fluoride is an azeotropic mixture.

15. A process for separating a halocarbon and hydrogen fluoride from a mixture containing a halocarbon and hydrogen fluoride which comprises adding water alone to a mixture comprising a halocarbon and hydrogen fluoride to thereby form a first phase rich in the halocarbon and a second phase rich in hydrogen fluoride and water; wherein the weight ratio of added water to hydrogen fluoride ranges from 3:2 to about 1:5 and wherein the weight ratio of water to hydrogen fluoride in the formed second phase ranges from about 3:2 to about 1:5.

16. The process of claim 15 wherein the halocarbon contains at least three carbon atoms.

17. The process of claim 16 wherein the halocarbon is a hydrofluorocarbon.

18. The process of claim 17 wherein the hydrofluorocarbon has three carbon atoms.

19. The process of claim 17 wherein the hydrofluorocarbon has four carbon atoms.

20. The process of claim 17 wherein the hydrofluorocarbon has five carbon atoms.

21. The process of claim 15 wherein the halocarbon comprises 1,1,1,3,3-pentafluoropropane.

22. The process of claim 15 wherein the halocarbon comprises 1,1,2,3,3-pentafluoropropane.

23. The process of claim 15 wherein the halocarbon comprises 1,1,1,2,2,5-hexafluorobutane.

24. The process of claim 15 further comprising the subsequent step of removing the first phase rich in the halocarbon from the second phase rich in the hydrogen fluoride and water.

25. The process of claim 24 further comprising the subsequent step of separating the hydrogen fluoride and water in the second phase.

26. The process of claim 15 wherein the separating is conducted at a temperature of from about 0 ^{o}C to about 100 ^{o}C.

27. The process of claim 15 wherein the mixture of halocarbon and hydrogen fluoride is an azeotropic mixture.

INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C07C17/38 C07C19/08

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 3 947 558 A (VAN EIJL A THEODORUS) 30 March 1976 cited in the application see claims	1,15
Y	DE 15 67 494 A (FARBWERKE HOECHST AG) 10 September 1970 see page 1; claims	1,15
Y	EP 0 583 551 A (SHOWA DENKO KK) 23 February 1994 cited in the application see claims	1,15

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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1

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Information on patent family members

Internal Application No
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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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